

**Remarks**

Claims 13-17 are pending in the above-identified application. By this Amendment, claims 13 and 14 have been cancelled, and claim 15 has been amended. Specifically, claim 15 has been amended to include the contents of cancelled claim 13 and to render claim 15 an independent claim. Because the amendment to claim 15 involves the incorporation therein of subject matter found in a previously considered claim, Applicants submit that the amendment does not raise new issues. Accordingly, Applicants respectfully request entry of this Amendment.

In the Office Action, claims 13 and 14 are rejected under 35 U.S.C. §102(e) as being anticipated by U.S. Patent 6,239,044 to Kashiwagi et al. ("Kashiwagi"); and claims 15-17 are rejected under 35 U.S.C. §103(a) as being unpatentable over Kashiwagi in view of U.S. Patent 6,516,143 to Toya et al. ("Toya").

In view of the amendments and remarks herein, Applicants respectfully request reconsideration and withdrawal of the rejections set forth in the Office Action.

**I. Rejection Under 35 U.S.C. §102(e)**

Claims 13 and 14 are rejected under 35 U.S.C. §102(e) as being anticipated by Kashiwagi.

In view of the cancellation of claims 13 and 14, Applicants submit that this rejection is now moot.

## **II. Rejection Under 35 U.S.C. §103(a)**

Claims 15-17 are rejected under 35 U.S.C. §103(a) as being unpatentable over Kashiwagi in view of Toya.

In a Claim for Foreign Priority filed with the instant application, the benefit of four Japanese applications was claimed, including the two listed below:

Japan 2000 – 157879 05/29/2000

Japan 2000 – 162950 05/31/2000.

The filing dates of the above two Japanese applications each precede the effective date of the Toya patent.

According to the Office Action, Applicants cannot rely upon the foreign priority papers to overcome this rejection because a translation of the papers has not been made of record. Applicants submit herewith English-language translations of the certified copies of the aforementioned Japanese applications, as well as a Statement that the translations of the certified copies are accurate. In view of the submission of these translations, Applicants respectfully submit that Toya is not available as a reference against the instant application.

The Office Action states that Kashiwagi differs from claims 15-17 in that the patent does not teach that the gas heating unit comprises a heating vessel defining a heating chamber packed with flow impeding members, and a carbon resistance heating member with a quartz cover sealing the resistance heating member surrounding the heating chamber. Toya was cited for teaching a gas heating unit comprising a heating vessel defining a heating chamber packed with flow impeding members and a carbon resistance

heating member with a quartz cover sealing the resistance heating member surrounding the heating chamber.

Because Toya is not a prior art reference relevant to Applicants' claimed invention, its teachings cannot be combined with Kashiwagi against the instant claims. Since, as acknowledged in the Office Action, Kashiwagi does not teach the features set forth in claims 15-17, Applicants respectfully submit that these claims would not have been obvious over Kashiwagi.

### **III. Conclusion**

In view of the amendments and remarks herein, Applicants respectfully request that the rejections set forth in the Office Action be withdrawn and that claims 15-17 be allowed.

Respectfully submitted,



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Enclosures: (1) English-language Translations of the Certified Copies of  
Japanese Application Nos. 157879 and 162950  
(2) Statements That the Translations of the Certified Copies Are Accurate

### LISTING OF CLAIMS

Claims 1-14 (cancelled)

Claim 15 (Currently Amended): A silicon dioxide film forming system ~~according to claim 13~~, comprising:

a reaction vessel defining a reaction chamber that can contain an object to be processed having a surface provided with at least a silicon layer;

a reaction chamber heating unit that heats the reaction chamber to a predetermined temperature;

a process gas supplying unit that supplies a process gas into the reaction chamber, the process gas containing a compound gas including hydrogen and chlorine, and oxygen gas; and

a gas heating unit, provided at the gas supplying unit, that heats the process gas to produce water before the process gas is supplied into the reaction chamber,  
wherein

the gas heating unit comprises:

a heating vessel defining a heating chamber packed with flow impeding members, and

a heating element surrounding the heating chamber; and

the heating element includes a resistance heating member and a ceramic cover sealing the resistance heating member therein.

Claim 16 (Original): A silicon dioxide film forming system according to claim 15,  
wherein

the resistance heating member is made of carbon with a high purity.

Claim 17 (Original): A silicon dioxide film forming system according to claim 15,  
wherein  
the ceramic cover is made of quartz.

Claims 18-31 (cancelled)

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application: May 29, 2000

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Applicant(s): TOKYO ELECTRON LIMITED

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[Document Name] SPECIFICATION

2000-157879

[Title of the Invention] METHOD OF FORMING OXYNITRIDE FILM AND SYSTEM  
FOR CARRYING OUT THE SAME

[Scope of Claims]

[Claim 1]

An oxynitride film forming method for forming an oxynitride film on the surface of an object to be processed by heating a reaction chamber that contains the object to be processed to a predetermined temperature and supplying a process gas consisting of dinitrogen oxide to the reaction chamber,

wherein

a process gas is heated to a temperature not lower than a reaction temperature at which an oxynitride film can be formed, and

the heated process gas is supplied to the reaction chamber simultaneously with setting the temperature of the reaction chamber at a temperature below the reaction temperature.

[Claim 2]

An oxynitride film forming method according to claim 1,

wherein

the process gas is heated to a temperature at which the process gas is pyrolyzed substantially completely, and the pyrolyzed gas is supplied to the reaction chamber.

[Claim 3]

An oxynitride film forming method according to claim 1 or 2,

wherein

the process gas is heated to 900°C or above, and

the reaction chamber is set to a temperature in a range of 750 to 850°C.

[Claim 4]

An oxynitride film forming method according to any one of claims 1 to 3,

wherein

the reaction chamber includes an inner tube that contains the object to be processed and an outer tube with a ceiling that surrounds the inner tube, and  
the process gas is supplied into the inner tube.

[Claim 5]

An oxynitride film forming system comprising:

a reaction chamber that can contain an object to be processed and includes a heating unit that can heat the reaction chamber to a predetermined temperature;

a supplying unit that can supply a process gas into the reaction chamber, the process gas consisting of dinitrogen oxide gas;

a heating unit, provided at the supplying unit, that can heat the process gas to a predetermined temperature;

a controller unit that can control the heating unit so as to heat the process gas to a temperature not lower than a reaction temperature at which an oxynitride film can be formed and control the reaction chamber heating unit so as to heat the reaction chamber to a temperature below a reaction temperature at which the process gas undergoes a reaction.

[Claim 6]

An oxynitride film forming system according to claim 5,

wherein

the controller controls the heating unit to heat the process gas to a temperature at which the process gas is pyrolyzed substantially completely.

[Claim 7]

An oxynitride film forming system according to claim 5 or 6,

wherein

the controller controls the heating unit to heat the process gas to 900°C or above, and to control the reaction chamber to a temperature in a range of 750 to 850°C.

[Claim 8]

An oxynitride film forming system according to any one of claims 5 to 7,

wherein

the reaction chamber includes an inner tube that contains the object to be processed and an outer tube with a ceiling that surrounds the inner tube, and

the supplying unit is adapted to supply the process gas into the inner tube

[Background of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a method of forming an oxynitride film and a system for carrying out the same. More specifically, the present invention relates to a method of forming an oxynitride film on an object to be processed, such as a semiconductor wafer, and a system for carrying out the same.

[0002]

[Description of the Related Art]

A semiconductor device fabricating process forms an insulating film on an object to be processed, such as a semiconductor wafer. This insulating film is used, for example, as a mask for impurity diffusion or ion implantation or as a source of diffusion of an impurity. A silicon oxynitride film is used occasionally as such an insulating film. Silicon oxynitride films, as compared with prevalently used silicon oxide films, have a high dielectric constant and have a high capability of preventing penetration by an impurity, such as boron.

[0003]

A silicon oxynitride film is formed on a surface of a semiconductor wafer by, for example, subjecting a semiconductor wafer to a thermal process. In this thermal process, a semiconductor wafer, such as a silicon wafer, is placed in a thermal processing system. Next, the semiconductor wafer is heated to a high temperature of, for example, 900°C. Then, a process gas, such as dinitrogen oxide gas ( $\text{N}_2\text{O}$  gas) is supplied into the thermal processing system for a predetermined time to form a silicon oxynitride film on the surface of the semiconductor wafer.

[0004]

On the other hand, the progressive miniaturization of semiconductor devices requires reduction of thickness of silicon oxynitride films. Generally, it is preferable to lower the process temperature in the thermal processing system to form silicon oxynitride

films of a small thickness, because the lowering of the process temperature is effective in reducing oxidation rate.

[0005]

[Problems to be Solved by the Invention]

However, if the process temperature is lowered, for example, from 900°C to 800°C or 750°C, nitrogen gas cannot satisfactorily be pyrolyzed and, consequently, it is difficult to form an oxynitride film having a desired nitrogen content.

[0006]

It is an object of the present invention to provide an oxynitride film forming method and an oxynitride film forming system capable of forming a thin oxynitride film having a desired nitrogen content.

[0007]

[Means for Solving the Problems]

In order to attain the above object, according to one feature of the present invention, an oxynitride film forming method comprises: a step of heating a reaction chamber to a predetermined temperature, the reaction chamber containing an object to be processed; a step of heating a process gas to a temperature not lower than a reaction temperature at which an oxynitride film can be formed, the process gas consisting of dinitrogen oxide gas; and a step of forming an oxynitride film on the object to be processed by supplying the heated process gas into the heated processing chamber; wherein the temperature to which the reaction chamber is heated in the reaction chamber heating step is set at a temperature below a temperature at which the process gas undergoes a reaction.

[0008]

According to the feature, the temperature of the reaction chamber is set below the reaction temperature of the process gas. Consequently, the oxidation rate by the process gas supplied into the reaction chamber is reduced and hence a thin oxynitride film can be formed. On the other hand, the process gas is heated in advance to a temperature not lower than the reaction temperature at which an oxynitride film can be formed, and is then supplied into the reaction chamber in a state suitable for oxynitriding. Consequently, an oxynitride film having a desired nitrogen content can be formed on the object to be processed.

[0009]

Preferably, the process gas is heated to a temperature at which the process gas is pyrolyzed substantially completely, in the gas heating step. In the case, the process gas can have a high nitrogen concentration, and hence an oxynitride film having a desired nitrogen content can be surely formed on the object to be processed.

[0010]

Preferably, the reaction chamber is heated to a temperature in a range of 750 to 850°C in the reaction chamber heating step, and the process gas is heated to 900°C or above in the gas heating step. When the process gas is heated at 900°C or above, the process gas is pyrolyzed substantially completely. In addition, a thin oxynitride film can be formed when the temperature of the reaction chamber is set in the range of 750 to 850°C.

[0011]

The reaction chamber includes an inner tube that can contain the object to be processed and an outer tube with a ceiling that surrounds the inner tube, and the process gas is supplied into the inner tube.

[0012]

According to another feature of the present invention, an oxynitride film forming system comprises: a reaction chamber that can contain an object to be processed and includes a heating unit that can heat the reaction chamber to a predetermined temperature; a supplying unit that can supply a process gas into the reaction chamber, the process gas consisting of dinitrogen oxide gas; a heating unit, provided at the supplying unit, that can heat the process gas to a predetermined temperature before the process gas is supplied into the reaction chamber; and a controller that can control the gas heating unit so as to heat the process gas to a temperature not lower than a reaction temperature at which an oxynitride film can be formed and control the heating unit so as to heat the reaction chamber to a temperature below a reaction temperature at which the process gas undergoes a reaction.

[0013]

According to the feature, by means of the controller, the temperature of the reaction chamber is controlled below the reaction temperature of the process gas. Consequently, the oxidation rate by the process gas supplied into the reaction chamber

is reduced and hence a thin oxynitride film can be formed. On the other hand, by means of the controller, the process gas is heated in advance to a temperature not lower than the reaction temperature at which an oxynitride film can be formed, and is then supplied into the reaction chamber in a state suitable for oxynitriding. Consequently, an oxynitride film having a desired nitrogen content can be formed on the object to be processed.

[0014]

Preferably, the controller is adapted to control the heating unit to heat the process gas to a temperature at which the process gas is pyrolyzed substantially completely. In the case, the process gas can have a high nitrogen concentration, and hence an oxynitride film having a desired nitrogen content can be surely formed on the object to be processed.

[0015]

Preferably, the controller is adapted to control the gas heating unit to heat the process gas to 900°C or above, and to control the reaction chamber heating unit to heat the reaction chamber to a temperature in a range of 750 to 850°C. When the process gas is heated at 900°C or above, the process gas is pyrolyzed substantially completely. In addition, a thin oxynitride film can be formed when the temperature of the reaction chamber is set in the range of 750 to 850°C.

[0016]

In addition, the reaction chamber includes an inner tube that contains the object to be processed and an outer tube with a ceiling that surrounds the inner tube, and the supplying unit is adapted to supply the process gas into the inner tube.

[0017]

[Best Mode for Carrying Out the Invention]

An oxynitride film forming method and a system for carrying out the same in an embodiment according to the present invention will be described as applied to forming silicon oxynitride films on semiconductor wafers (objects to be processed) by using a batch-type vertical thermal processing system shown in Fig. 1.

[0018]

Referring to Fig. 1, a thermal processing system 1 has a substantially cylindrical reaction tube 2 set in a vertical posture. The reaction tube 2 is a double-wall structure

having an inner tube 3 and an outer tube 4 having a closed upper end. The outer tube 4 with a ceiling surrounds the inner tube 3 so as to form an annular space of a predetermined thickness between the inner tube 3 and the outer tube 4. The inner tube 3 and the outer tube 4 are formed of a heat-resisting material, such as quartz (crystal).

[0019]

A cylindrical manifold 5 made of a stainless steel (SUS) is disposed under the outer tube 4. A lower end of the outer tube 4 is joined hermetically to the manifold 5. The inner tube 3 is supported on a support ring 6, which is formed integrally with the manifold 5 and projecting from the inner circumference of the manifold 5.

[0020]

A lid 7 is disposed below the manifold 5. A boat elevator 8 is adapted to move the lid 7 vertically. When the lid 7 is raised by the boat elevator 8, an open lower end of the manifold 5 is closed.

[0021]

A wafer boat 9 made of, for example, quartz is mounted on the lid 7. The wafer boat 9 can hold a plurality of objects to be processed, such as semiconductor wafers 10, at predetermined vertical intervals.

[0022]

A heat insulating member 11 surrounds the reaction tube 2. A reaction tube heater 12, such as a resistance-heating element, is provided on an inner circumference of the heat insulating member 11.

[0023]

A gas supply pipe 13 is connected to a side wall of the manifold 5. The gas supply pipe 13 is connected to a part of the side wall of the manifold below the support ring 6 so as to open into a space defined by the inner tube 3. Thus, a process gas is adapted to be supplied through the gas supply pipe 13 into the inner tube 3 of the reaction tube 2.

[0024]

A discharge port 14 is formed in a part of the side wall of the manifold 5 on a level above that of the support ring 6. The discharge port 14 opens into the space between the inner tube 3 and the outer tube 4 of the reaction tube 2. A process gas is

supplied through the gas supply pipe 13 into the inner tube 3 and a film forming process is started. Reaction products produced by the film forming process flow through the space between the inner tube 3 and the outer tube 4 and are discharged from the thermal processing system 1 through the discharge port 14.

[0025]

A gas heating unit 15 provided with, for example, a resistance heating element is combined with the gas supply pipe 13. The heating unit 15 is adapted to heat the process gas being dinitrogen oxide ( $\text{N}_2\text{O}$ ) gas that flows through the heating unit 15, to a predetermined temperature. The heated process gas flows through the gas supply pipe 13 into the reaction tube 2.

[0026]

A controller 16 is connected to the boat elevator 8, the reaction tube heater 12, the gas supply pipe 13 and the heating unit 15. The controller 16 comprises a microprocessor, a process controller or the like. The controller 16 is adapted to measure temperatures and pressures of predetermined parts of the thermal processing system 1, and provide control signals or the like to the aforesaid components on the basis of measured data, in order to control them.

[0027]

An oxynitride film forming method that uses the thermal processing system 1 will be described as applied to forming silicon oxynitride films on semiconductor wafers 10. With respect to the following description, the controller 16 controls operations of the aforesaid components of the thermal processing system 1.

[0028]

The boat elevator 8 lowers the lid 7, and the wafer boat 9 holding the semiconductor wafers 10 is placed on the lid 7. Then, the boat elevator 8 raises the lid 7 to load the wafer boat 9 holding the semiconductor wafers 10 into the reaction tube 2. Thus, the semiconductor wafers 10 are held inside the inner tube 3 of the reaction tube 2 and the reaction tube 2 is sealed.

[0029]

The heating unit 15 is heated to a predetermined temperature by a heater, not shown.



The process gas was supplied through the heating unit 15 while the heating unit 15 was heated at 750°C, 900°C or 1000°C, so that the concentrations of the components of the process gas heated by the heating unit 15 were measured to examine the effect of the temperature of the heating unit 15. The measured concentrations of the components of the process gas in the respective conditions are shown in Fig. 2.

[0030]

As obvious from Fig. 2, about half the dinitrogen oxide was not pyrolyzed at 750°C. At 900°C, 8% of the dinitrogen oxide was not pyrolyzed. At 1000°C, 1% of the dinitrogen oxide was not pyrolyzed. It was found that nitrogen, oxygen, nitrogen monoxide and nitrogen dioxide or the like are produced by the pyrolysis of dinitrogen oxide. Thus, it was confirmed that dinitrogen oxide can be substantially completely pyrolyzed when the heating unit 15 is heated at a temperature not lower than 900°C.

[0031]

The nitrogen concentration increased from 28% to 40% when the temperature was raised from 750°C to 900°C. The nitrogen concentration greatly increased to 47% when the temperature was raised to 1000°C. As a result, a large amount of nitrogen can be supplied to the semiconductor wafers 10. On the other hand, oxygen concentration, as compared with nitrogen concentration, did not increase significantly when the temperature was raised from 750°C through 900°C to 1000°C, because the ratio of decrease of oxygen is greater than that of nitrogen since nitrogen monoxide and nitrogen dioxide are produced from nitrogen and oxygen. Thus, it was confirmed that the nitrogen concentration of the process gas increases and the increase of the oxygen concentration is not as great as that of nitrogen concentration when dinitrogen oxide is heated to temperatures not lower than 900°C. That is, because the increase of the nitrogen concentration of the process gas is relatively large when the process gas is heated to temperatures not lower than 900°C, a large amount of nitrogen can be supplied to the semiconductor wafers 10.

[0032]

Accordingly, the heating unit 15 is preferably heated to a temperature of 900°C or above, at which dinitrogen oxide, i.e., the process gas, is substantially completely pyrolyzed. However, since only 1% of the dinitrogen oxide is not pyrolyzed when the dinitrogen oxide

is heated at 1000°C, further pyrolysis of the dinitrogen oxide cannot be expected even if the dinitrogen oxide is heated to a higher temperature of, for example, 1100°C. Thus, it is most preferable to heat the heating unit 15 to about 1000°C. In this embodiment, the heating unit 15 is heated at 1000°C.

[0033]

The reaction tube heater 12 heats the interior of the reaction tube 2 to a predetermined temperature, such as 800°C, lower than the temperature to which the process gas is heated. The temperature of the reaction tube 2 is determined according to thickness of a silicon oxynitride film to be formed, and is a temperature lower than the temperature to which the process gas is heated and high enough to form a silicon oxynitride film. Preferably, the temperature of the reaction tube 2 is, for example, in a range of 750 to 850°C. The thickness of the silicon oxynitride film is dependent on the temperature of the reaction tube 2 and the duration of supply of the process gas. A silicon oxynitride film having a predetermined nitrogen content and a desired thickness cannot be formed if the temperature of the reaction tube 2 is below 750°C. On the other hand, an oxide film grows greatly and the nitrogen content of the silicon oxynitride film decreases if the temperature of the reaction tube 2 is above 850°C. In addition, if the reaction tube 2 is heated to a temperature not higher than 750°C and the process gas is supplied for a long time, in some cases, the amount of nitrogen diffused in the film may be saturated. Therefore, it is more preferable that the temperature of the reaction tube 2 is in a range of 800 to 850°C.

[0034]

After the reaction tube 2 has been sealed, the reaction tube 2 is evacuated to a predetermined pressure of, for example, 95760 Pa (720 Torr). Then, dinitrogen oxide gas is supplied, for example, at 5 l/min (5 slm) into the gas supply pipe 13, maintaining the pressure in the reaction tube 2 at 95760 Pa (720 Torr).

[0035]

The heating unit 15 pyrolyzes the dinitrogen oxide gas introduced into the gas supply pipe 13. The pyrolyzed process gas is supplied through the gas supply pipe 13 onto the semiconductor wafers 10 placed inside the inner tube 3.

[0036]

In the reaction tube 2, surfaces of the semiconductor wafers 10 are oxynitrided by the pyrolyzed process gas. The process gas is supplied for a predetermined time of, for example, 15 min, silicon oxynitride films are formed on the semiconductor wafers 10, respectively. Fig. 3 shows thicknesses and maximum nitrogen contents (Peak N) of silicon oxynitride films formed on semiconductor wafers. The maximum nitrogen content (Peak N) is the greatest one of respective nitrogen contents of different parts of a silicon oxynitride film, and is a value that serves as a criterion on which the estimation of the nitrogen content of the silicon oxynitride film is based. Comparative silicon oxynitride films of thicknesses and maximum nitrogen contents (Peak N) as shown in Fig. 3 were formed by silicon oxynitride film forming methods, wherein the process gas was not heated by the heating unit 15 and the reaction tube 2 was heated at 800°C (Comparative Example 1) and 900°C (Comparative Example 2), respectively.

[0037]

As shown in Fig. 3, the silicon oxynitride film formed by the silicon oxynitride film forming method of the present embodiment had a maximum nitrogen content (Peak N) of 2.24 atomic percent even if the temperature of the reaction tube 2 was lowered from 900°C (conventional temperature) to 800°C. Thus, a substantially equal value to the maximum nitrogen content (Peak N) of 2.33 atomic percent of the silicon oxynitride film formed by the silicon oxynitride film forming method in the Comparative example 1 wherein the reaction tube 2 is heated to 900°C, which may be due to the increase of the nitrogen concentration of the process gas resulting from the pyrolysis of dinitrogen oxide by the heating unit 15.

[0038]

The reduction of the temperature of the reaction tube 2 to 800°C caused the reduction of oxidation rate and, consequently, the silicon oxynitride film as thin as 2 nm could be formed. That is, the silicon oxynitride film forming method of the present invention was able to form a thin silicon oxynitride film without reducing maximum nitrogen content, whereas the silicon oxynitride film formed by the silicon oxynitride film forming method in the Comparative example 2, wherein the reaction tube 2 is heated to

800°C, was thin but had a low maximum nitrogen content. In addition, since the heating unit 15 pyrolyzed the dinitrogen oxide substantially completely, the silicon oxynitride film had an excellent intrasurface thickness uniformity.

[0039]

The supply of the process gas through the gas supply pipe 13 is stopped after desired silicon oxynitride films have been formed on the surfaces of the semiconductor wafers 10. The gas prevailing in the reaction tube 2 is discharged through the discharge port 14 and the pressure in the reaction tube 2 returns to the atmospheric pressure. Then, the boat elevator 8 lowers the lid 7 to unload the wafer boat 9 (semiconductor wafers 10) from the reaction tube 2.

[0040]

The temperature of the inner tube 3 was measured to examine the effect of supplying the process gas heated at the temperature (1000°C) higher than the temperature (800°C) of the reaction tube 2 into the reaction tube 2 on the temperature of the inner tube 3. Temperature was measured at four measuring points T1 to T4 on the inner circumference of the inner tube 3, as shown in Fig. 1. Measured temperatures are shown in Fig. 4. Measured temperatures of the inner tube 3 in Comparative Example 3 wherein the process gas is not heated are also shown in Fig. 4. As obvious from Fig. 4, whereas the temperature of the process gas used in the silicon oxynitride film forming method of the present invention and that of the same used in the silicon oxynitride film forming method in Comparative Example 3 were different, the temperatures of parts of the inner circumference of the inner tube 3 during the execution of the silicon oxynitride film forming method of the present invention were substantially equal to those of the same parts of the inner tube 3 during the execution of the silicon oxynitride film forming method in Comparative example 3. Thus, it was confirmed that the supply of the heated process gas into the reaction tube 2 does not disturb the uniformity of temperature distribution in the reaction tube 2.

[0041]

As apparent from the foregoing description, according to the present embodiment, the process gas is heated to 1000°C by the heating unit 15, and the substantially completely

pyrolyzed process gas is supplied into the reaction tube 2. Consequently, the nitrogen concentration of the process gas can be increased and a large amount of nitrogen can be supplied onto the semiconductor wafers 10. Therefore, even if the temperature of the reaction tube 2 is reduced from 900°C to 800°C, a silicon oxynitride film having a maximum nitrogen content (Peak N) substantially equal to that of a silicon oxynitride film formed by the silicon oxynitride film forming method that heats the reaction tube at 900°C can be formed. In addition, since the temperature of the reaction tube 2 is reduced from 900°C to 800°C, a very thin silicon oxynitride film can be formed. As the result, the silicon oxynitride film is able to form a thin film without reducing maximum nitrogen content.

[0042]

Modifications of the silicon oxynitride film forming method in the first embodiment such as the following case are possible.

[0043]

The foregoing silicon oxynitride forming method in the present embodiment subjects the semiconductor wafers 10 directly to the oxynitriding process to form the silicon oxynitride film on the semiconductor wafers 10. However, semiconductor wafers 10 having surfaces coated respectively with silicon dioxide films may be subjected to the oxynitriding process to form silicon oxynitride films on the semiconductor wafers.

[0044]

Semiconductor wafers 10 having surfaces coated respectively with, for example, 3 nm thick silicon dioxide films were held on the wafer boat 9. The pressure in the reaction tube 2 was set at 95760 Pa (720 Torr), the heating unit 15 was heated to 900°C or 1000°C. The reaction tube 2 was heated to 750°C, 800°C or 850°C. Dinitrogen oxide gas was supplied through the gas supply pipe 13 at 5 l/min (5 slm) for 15 min to form silicon oxynitride films on the semiconductor wafers 10, respectively, by subjecting the silicon dioxide films to an oxynitriding process. Silicon oxynitride films were also formed on the semiconductor wafers 10 by subjecting the silicon dioxide films to an oxynitriding process in the same manner in cases wherein the temperature of the heating unit 15 is 1000°C and the process gas is supplied for 30 min, and cases wherein the heating unit 15 is not heated. Fig. 5 shows thickness increment and maximum nitrogen content (Peak N) of

the thus formed silicon oxynitride films.

[0045]

As obvious from Fig. 5, heating the process gas by the heating unit 15 can increase maximum nitrogen content (Peak N). The thicknesses are substantially the same when the processes are the same in the temperature of the reaction tube 2 and reaction time. Thus, a very thin silicon oxynitride film having a desired nitrogen content can be formed by heating the process gas by the heating unit 15 and by heating the reaction tube 2 to a reduced temperature.

[0046]

For example, a very thin silicon oxynitride film having a maximum nitrogen content equal to that of a silicon oxynitride film (thickness increment: 1.01 nm, maximum nitrogen content (Peak N): 0.52 atomic percent) formed by heating the reaction tube 2 to 850°C and without heating the process gas by the heating unit 15 can be formed by heating the process gas to 900°C by the heating unit 15 and by heating the reaction tube 2 to 750°C. The silicon oxynitride film thus formed can have a thickness increment of 0.29 nm, which is about 1/4 of the thickness increment.

[0047]

When the respective temperatures of the heating unit 15 and the reaction tube 2 were 1000°C and 750°C and the reaction time was increased from 15 min to 30 min, the maximum nitrogen content (Peak N) decreased from 1.13 atomic percent to 0.78 atomic percent. It may be considered that, in some cases, the amount of nitrogen diffused in the film is saturated and, consequently, the thickness increases, when the temperature of the reaction tube 2 is comparatively low and the reaction time is long. Thus, it is preferable to heat the reaction tube 2 to a temperature not lower than 800°C when the reaction time is as long as 30 min.

[0048]

The oxynitride film forming system in the first embodiment is a batch-type vertical thermal processing system provided with the reaction tube 2 of a double-wall structure consisting of the inner tube 3 and the outer tube 4. The present invention is not limited thereto, and is applicable to various processing systems for forming an

oxynitride film on an object to be processed. Further, the object to be processed is not limited to a semiconductor wafer and the present invention is applicable to processing various objects, such as glass substrates for forming LCDs.

[0049]

[Advantages of the Invention]

As described above, according to the present invention, a thin oxynitride film containing a desired amount of nitrogen can be formed.

[Brief Description of the Drawings]

[Fig. 1]

A schematic view of a thermal processing system in an embodiment.

[Fig. 2]

A table of concentrations of component gases of respective heated process gases in the embodiment.

[Fig. 3]

A table of thicknesses and maximum nitrogen contents (Peak N) of respective silicon oxynitride films in the embodiment.

[Fig. 4]

A table of temperatures of an inner tube when a heated process gas is supplied into the inner tube.

[Fig. 5]

A table of increments in the thicknesses and maximum nitrogen contents (Peak N) of respective silicon oxynitride films.

[Reference Signs]

- 1: Thermal processing system
- 2: Reaction tube
- 3: Inner tube
- 4: Outer tube
- 10: Semiconductor wafer

12: Reaction tube heater

13: Gas supply pipe

15: Heating unit

16: Controller



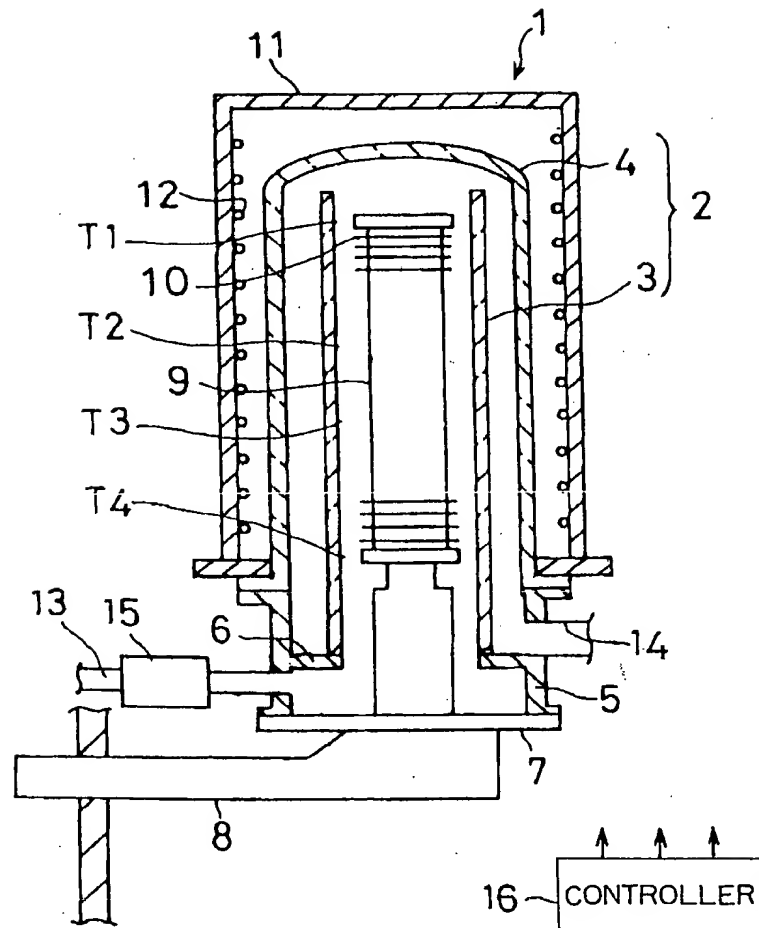


Fig. 1

TEMPERA- TURE OF HEATING UNIT \ COM- PONENT	N <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>	NO	NO <sub>2</sub>
1 0 0 0 °C	1	4 7	1 9	0 . 3	3 . 0
9 0 0 °C	8	4 0	1 7	0 . 2	2 . 0
7 5 0 °C	5 4	2 8	1 3	0 . 0 5	0 . 5

(%)

Fig. 2

	FILM THICKNESS	P e a k N VOLUME
EMBODIMENT	2 . 0 0 n m	2 . 2 4 a t o m i c %
COMPARATIVE EXAMPLE 1	3 . 3 6 n m	2 . 3 3 a t o m i c %
COMPARATIVE EXAMPLE 2	2 . 0 0 n m	0 . 8 7 a t o m i c %

Fig. 3

	T 1	T 2	T 3	T 4
EMBODIMENT	7 9 8 . 6	8 0 0 . 2	8 0 0 . 1	8 0 2 . 6
COMPARATIVE EXAMPLE 3	7 9 8 . 4	8 0 0 . 1	7 9 9 . 9	8 0 1 . 8

(°C)

Fig. 4

PROCESSING CONDITION		TEMPERATURE OF REACTION TUBE	7 5 0 °C	8 0 0 °C	8 5 0 °C
HEATING UNIT 900 °C  REACTION TIME 15 MIN	THICKNESS INCREMENT		0 . 2 9	0 . 5 0	0 . 9 0
	PEAK N VOLUME		0 . 5 5	1 . 0 5	1 . 5 3
HEATING UNIT 1000 °C  REACTION TIME 15 MIN	THICKNESS INCREMENT		0 . 2 8	0 . 4 7	0 . 8 8
	PEAK N VOLUME		1 . 1 3	1 . 2 4	1 . 6 6
HEATING UNIT 1000 °C  REACTION TIME 30 MIN	THICKNESS INCREMENT		0 . 3 6	0 . 7 5	1 . 0 9
	PEAK N VOLUME		0 . 7 8	1 . 7 2	1 . 8 3
HEATING UNIT NOT HEATED  REACTION TIME 15 MIN	THICKNESS INCREMENT		0 . 3 0	0 . 5 4	1 . 0 1
	PEAK N VOLUME		0 . 2 1	0 . 3 6	0 . 5 2

( THICKNESS INCREMENT : nm, PEAK N VOLUME : atomic % )

Fig. 5

[Document Name]     ABSTRACT

[Abstract]

[Means to Solve Problems]

To provide an oxynitride film forming method and an oxynitride film forming system capable of forming a thin oxynitride film having a desired nitrogen content.

[Means for Solving the Problems]

A thermal processing system 1 has a reaction chamber 2 for forming a silicon oxynitride film on a surface of a semiconductor wafer 10 and a gas supply pipe 13 connected to the reaction chamber 2. The gas supply pipe 13 is provided therein a heating unit 15 for heating a process gas. The heating unit 15 heats the process gas up to 1000°C, the heated process gas being supplied to the reaction chamber 2 through the gas supply pipe 13, and sets the temperature of the reaction chamber 2 to 800°C.

[Selected Drawing]

Fig. 1

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This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number: Patent Application No. 2000-162950

Applicant(s): TOKYO ELECTRON LIMITED

April 20, 2001

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The Commissioner of The Patent Office

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Specification 1

Drawing(s) 1

Abstract 1

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[Title of the Invention] METHOD OF OXIDATION PROCESSING AND SYSTEM  
FOR CARRYING OUT THE SAME

[Scope of Claims]

[Claim 1]

An oxidation processing method comprising:

a step of forming a silicon oxide film by bringing an object to be processed into a reaction vessel, the object to be processed being provided with a silicon layer formed at least on the surface thereof, heating the interior of the reaction vessel to a predetermined process temperature, and supplying a process gas containing a compound gas including hydrogen and chlorine, and an oxygen gas into the reaction vessel,

wherein

energy is supplied to the process gas to be supplied into the reaction vessel to generate a small amount of water.

[Claim 2]

An oxidation processing method according to claim 1,

wherein

a step energizing the process gas generates water in some extent that the generation of water is not promoted any further by a process temperature in the reaction vessel.

[Claim 3]

An oxidation processing method according to claim 1,

wherein

the step of energizing the process gas is a step of heating the process gas.

[Claim 4]

An oxidation processing method according to claim 3,

wherein

the temperature at which the process gas to be supplied into the reaction vessel is heated is higher than the process temperature in the reaction vessel.

[Claim 5]

An oxidation processing method according to claim 3 or 4,  
wherein

the step of heating the process gas to be supplied into the reaction vessel is carried out in a heating unit provided at a gas supply pipe for supplying gasses into the reaction vessel.

[Claim 6]

An oxidation processing method according to any one of claims 1 to 5,  
wherein

the compound gas containing hydrogen and chlorine is a hydrogen chloride gas.

[Claim 7]

An oxidation processing method according to any one of claims 1 to 6,  
wherein

the step of forming a silicon oxide film is carried out by holding a number of objects to be processed on a holder in a tier-like manner and then brought into a reaction tube set in a vertical posture.

[Claim 8]

An oxidation processing system for forming a silicon oxide film by oxidizing a silicon layer on the surface of the object to be processed, comprising:

a thermal processing unit that can oxidize the object to be processed by bringing the object to be processed into the reaction vessel, heating the interior of the reaction vessel to a predetermined process temperature, and supplying the process gas containing a compound gas including hydrogen and chlorine, and an oxygen gas into the reaction vessel,

a gas supply pipe that can supply the process gas into the reaction vessel, and

a heating unit provided at the gas supply pipe that can generate a small amount of water by heating the process gas to be supplied into the reaction vessel.

[Claim 9]

An oxidation processing system according to claim 8 further comprising a thermal processing unit, which is a vertical thermal processing unit that can hold a number of objects to be processed on the holder in a tier-like manner and then bring the objects to

be processed into the reaction vessel, and heat the interior of the reaction vessel to a predetermined temperature by a heating means surrounding the reaction vessel.

[Claim 10]

An oxidation processing system according to claim 8 or 9,

wherein

the heating unit comprises a heating chamber provided with flow impeding members that can heat the process gas and a heating element surrounding the heating chamber formed by sealing resistance heating members scarcely containing metal impurities into a ceramic.

[Claim 11]

An oxidation processing system according to claim 10,

wherein

the resistance heating member is made of a carbon material with a high purity.

[Claim 12]

An oxidation processing system according to claim 10 or 11,

wherein

the ceramic is made of quartz.

[Background of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a method of oxidation processing to form a silicon oxide film and a system for carrying out the same.

[0002]

[Description of the Related Art]

Methods of forming a silicon oxide film ( $\text{SiO}_2$  film) on each of a plurality of semiconductor wafers (hereinafter referred to simply as "wafers") placed in a batch-processing furnace by oxidizing a silicon film on each wafer are classified into: dry oxidation methods that use oxygen gas ( $\text{O}_2$  gas) and hydrogen chloride gas ( $\text{HCl}$  gas); and wet oxidation methods that produce steam by holding oxygen gas and hydrogen gas

(H<sub>2</sub>) by an external device and that supply the steam and oxygen gas into a reaction tube. A suitable oxidation method is selected according to desired film quality.

[0003]

The dry oxidation methods oxidize a silicon film with oxygen gas and remove impurities from the surface of the wafer by means of gettering-effect of chloride. More concretely, a wafer boat holding a plurality of wafers in a tier-like manner is carried into a vertical reaction tube, a process atmosphere in the reaction tube is heated by a heating element surrounding the reaction tube, a process gas of an ordinary temperature including oxygen gas and hydrogen chloride gas is supplied through a ceiling part of the reaction tube into the reaction tube, and the process atmosphere is exhausted through a lower part of the reaction tube.

[0004]

[Problems to be Solved by the Invention]

Higher process temperatures are more apt to produce a defect called a slip. In addition, it is preferable to avoid thermally affecting underlying films and to reduce energy consumption. Therefore, various studies have been made to reduce the process temperature.

[0005]

Since a diameter of the wafer is increasing progressively, thickness uniformity of a film formed on the surface of the wafer, i.e., intrasurface thickness uniformity becomes worse when the process temperature is reduced. In addition, thickness difference between films formed on the surfaces of the wafers, i.e., interwafer thickness uniformity also becomes worse.

[0006]

It has been found, through examinations of relation between the position of a wafer on a wafer boat and the thickness of a film formed on the same wafer, that the thickness uniformity of films formed on wafers held in an upper part of the wafer boat is worse than that of films formed on wafers held in a lower part of the wafer boat. The inventors of the present invention infer that dependence of thickness uniformity on the position of the wafer on the wafer boat is due to the following reasons. Figs. 7(a) to 7(c) show typically a flow of a gas over a wafer W, a temperature of the wafer W and a thickness

of a film formed on the wafer W, respectively. Oxygen gas and hydrogen chloride gas flow from a periphery (edge) of the wafer W toward a center of the same. Then, oxygen gas oxidizes silicon on the wafer W as the same flows along the surface of the wafer W. Since the wafer W dissipates heat through a peripheral part thereof, the temperature of the wafer W increases toward the center of the wafer W. High temperature promotes the oxidation, and hence silicon on a central part of the wafer W is oxidized at an oxidation rate higher than that at which silicon on a peripheral part is oxidized. Consequently, even if the film is formed in a highly uniform thickness, there is a tendency for a part of the film on a central part of the wafer W to be thicker than a part of the same on a peripheral part:

[0007]

Although it is only a small amount, interaction between hydrogen, which has been produced through decomposition of hydrogen chloride, and oxygen produces steam. The gas around an upper part of the wafer boat is not heated sufficiently. Thus, the temperature of the gas rises as the same flows from the periphery toward the center of the wafer W. Consequently, the amount of steam produced around the center of the wafer W is greater than that of steam produced around the periphery of the wafer W. The steam is effective in increasing the oxide film. Thus, the difference between the amount of steam produced around the peripheral part of the wafer W and that of steam produced around the central part of the wafer W greatly affects the difference between the thickness of a part of the film formed on the peripheral part of the wafer W and that of a part of the film formed on the central part of the wafer W. Consequently, the thickness of the part of the film on the central part of the wafer W is further increased so that the thickness of the film formed on the wafer W has a distribution of an upward convex curve, that is, the uniformity of the film thickness becomes worse. Since the temperature of the gas increases as the gas flows toward the lower part of the reaction tube, the above steam generating reaction is substantially equilibrated around the lower part of the wafer boat. That is, the gas is decomposed completely and all the possible amount of steam is produced before the gas flows along the wafers W. Therefore, substantially the same amount of steam exists around the peripheral part of the wafer W and around the central part of the wafer W as the process gas flows from the periphery toward the center of the wafer W

and, consequently, the film is formed in a highly uniform thickness. Thus, it is inferred that the uniformity of the thickness of the films formed on the wafers held in the upper part of the wafer boat is considerably bad, and the difference between the thickness of the films formed on the wafers held in the upper part of the wafer boat and that of the films formed on the wafers held in the lower part of the wafer boat is great. Accordingly, it is difficult to lower the process temperature at the present.

[0008]

The present invention was made under the above circumstances and the object thereof is to provide a technique capable of obtaining thickness uniformity of oxide films when objects to be processed are under the dry oxidation and contributing to reduction of process temperature.

[0009]

[Means for Solving the Problems]

The oxidation processing method according to the present invention comprises:

a step of forming a silicon oxide film by bringing an object to be processed into a reaction vessel, the object to be processed being provided with a silicon layer formed at least on the surface thereof, heating the interior of the reaction vessel to a predetermined process temperature, and supplying a process gas containing a compound gas including hydrogen and chlorine, and an oxygen gas into the reaction vessel,

wherein

energy is supplied to the process gas to be supplied into the reaction vessel to generate a small amount of water.

[0010]

The step of energizing the process gas is, for example, a step of generating water in some extent that the generation of water is not promoted any further by a process temperature in the reaction vessel. This step is a step of heating the process gas by means of, for example, a heating unit provided at a gas supply pipe. In the case, the process gas is preferably heated to a temperature that is higher than the temperature at which the reaction vessel is heated. For example, the compound gas including hydrogen and chlorine is a hydrogen chloride gas.

[0011]

For example, there is provided an oxidation processing system comprising: a thermal processing unit that can oxidize an object to be processed by bringing the object to be processed into the reaction vessel, heating the interior of the reaction vessel to a predetermined process temperature, and supplying the process gas containing a compound gas including hydrogen and chlorine, and an oxygen gas into the reaction vessel, a gas supply pipe that can supply the process gas into the reaction vessel, and a heating unit provided at the gas supply pipe that can generate a small amount of water by heating the process gas to be supplied into the reaction vessel. As a thermal processing unit, for example, a vertical thermal processing unit that can hold a number of objects to be processed on the holder in a tier-like manner and then bring the objects to be processed into the reaction vessel, and heat the interior of the reaction vessel to a predetermined temperature by a heating element surrounding the reaction vessel.

[0012]

Preferably, the heating unit comprises a heating vessel provided with flow impeding members that can heat the process gasses and the heating element unit consisting of resistance heating members scarcely containing impurities, which surrounds the heating vessel, and a heating element formed by sealing a carbon material with a high purity into a ceramic such as quartz.

[0013]

[Best Mode for Carrying Out the Invention]

Fig. 1 is an example of an oxidation processing system used to carryout the oxidation processing method according to the present invention. The oxidation processing system comprises a vertical thermal processing unit 1 and a heating unit 2 that can heat process gasses to be supplied into the vertical thermal processing unit 1. The structure of the vertical thermal processing unit 1 will be described. As shown in Figs. 1 and 2, the vertical thermal processing unit 1 comprises a vertical thermal processing furnace 3, a wafer boat 4 as a wafer holder, a boat elevator 40 for vertically moving the wafer boat 4, and a gas supply pipe 5 and an exhaust pipe 30 connected to the thermal processing furnace 3.



[0014]

The vertical thermal processing furnace 3 includes a reaction tube 31, i.e., a reaction vessel, made of, for example, quartz, a heating element 32 provided with a resistance heating element and surrounding the reaction tube 31, and a holding vessel 33 interposed between the reaction tube 31 and the heating element 32 supported on a heat insulating member 34. The reaction tube 31 has an open lower end and a top wall 31a. A gas diffusing plate 31c provided with a plurality of holes 31b is disposed in the reaction tube 31 at a position at a short distance below the top wall 31a. The gas supply pipe 5 extends through the heat insulating member 34, bends at right angle at a position on the inner side of the heat insulating member 34, extends upright through a space between the reaction tube 31 and the holding vessel 33 and extends into a space between the top wall 31a of the reaction tube 31 and the gas diffusing plate 31c.

[0015]

As shown in Fig. 1, the wafer boat 4 has a top plate 41, a bottom plate 42 and a plurality of support bars 43 extended between the top plate 41 and the bottom plate 42. Each of the support bars 43 is provided with horizontal grooves formed in a vertical direction to hold wafers W therein. The wafer boat 4 is mounted on a heat insulating cylinder 45 placed on a lid 44 for closing the open lower end 35 of the reaction tube 31. The heat insulating cylinder 45 is supported on a turntable 46 connected to a shaft 47. The shaft 47 is adapted to be driven for rotation by a driving unit M disposed on the boat elevator 40, to rotate the turntable 46 supporting the wafer boat 4 into and out of the thermal processing furnace 3.

[0016]

Referring to Fig. 3, the heating unit 2 is placed in a part of the gas supply pipe 5 extending outside the vertical thermal processing unit 1. The heating unit 2 comprises a heating pipe 21 made of, for example, transparent quartz defining a heating chamber, a heating element 22 helically wound around the heating pipe 21, and a cylindrical heat insulating member 23 covering the heating pipe 21 and the heating element 22. A cooling water passage 24 is formed in the heat insulating member 23. A cooling medium, such as cooling water, is passed through the cooling water passage 24. For example, many

transparent quartz beads 20 as flow impeding members are packed in the heating pipe 21. The quartz beads exert resistance against the flow of the gas. Consequently, the quartz beads are heated and the gas flows touching the heated quartz beads, whereby the gas is heated efficiently.

[0017]

The heating element 22 is carbon braid formed by braiding a plurality of carbon fiber strands of a high purity scarcely containing metallic impurities and the carbon braid is sealed in a ceramic member such as a quartz tube. Electric power is supplied through a cable 25 to the heating element 22 to generate heat. In addition, numeral 26 denotes a temperature sensor, which is a thermocouple.

[0018]

A valve V0 is placed in a part of the gas supply pipe 5 on a downstream side of the heating unit 2, and branch pipes 51 and 52 are connected to an oxygen gas source 53 and a hydrogen chloride gas source 54, respectively. V1 and V2 are valves, and MF1 and MF2 are mass flow controllers, i.e., flow controllers for controlling the flow rate of the gas. Preferably, the heating unit 2 is disposed as close to the thermal processing furnace 3 as possible to prevent the heated gas from cooling before flowing into the thermal processing furnace 3.

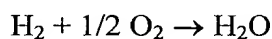
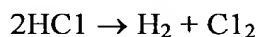
[0019]

Next, the operation of the silicon dioxide film forming system in the second embodiment will be described. A plurality of wafers W, such as sixty wafers W, each having a surface provided with a silicon layer, are held on the wafer boat 4 in a tier-like manner. Then, the boat elevator 40 carries the wafer boat 4 into the reaction tube 31 that has been heated beforehand at a predetermined temperature by the heater 32, and the open lower end 35 as the intake of the furnace is closed hermetically by the lid 44 (state shown in Fig. 1). Subsequently, the interior of the reaction tube 31 is heated to a predetermined process temperature of, for example, 800°C. In the step of loading the wafers W into the reaction tube 31 and the step of heating the interior of the reaction tube 31, nitrogen gas containing a small amount of oxygen gas is supplied through a gas supply pipe, not shown, into the reaction tube 31. Thereafter, the supply of nitrogen gas is stopped and the gas

remaining in the reaction tube 31 is discharged through the exhaust pipe 30 by an evacuating device, not shown, to evacuate the reaction tube 31 to a low negative pressure. An oxidation process is started after the temperature of the wafers W has stabilized.

[0020]

On the other hand, the heating unit 2 disposed outside the vertical thermal processing unit 1 is energized to heat the interior of the heating pipe 21 to, for example, 1000°C. The valve V0 is opened to pass a process gas containing oxygen gas and hydrogen chloride gas through the heating pipe 21. The process gas is heated at about 1000°C as the same flow through gaps between the transparent quartz beads 20 touching the transparent quartz beads 20. It is considered that the oxygen gas and the hydrogen chloride gas of the process gas may undergo chemical reactions expressed by the following reaction formulas, and that a very small amount of steam on the order of several hundreds parts per million may be generated.



The thus heated process gas flows into the thermal processing furnace 3. The process gas is then heated while flowing up inside the holding pipe 33 into an upper part of the reaction tube 31. Then, the process gas flows through the holes 31b into a processing region in the reaction tube 31, and is discharged through the exhaust pipe 30 connected to a lower part of the reaction tube 31. The process gas flows into spaces between the stacked wafers W. The oxygen gas contained in the process gas oxidizes the silicon layers on the surfaces of the wafers W to form silicon dioxide films. Steam contained in the process gas of a small concentration promotes the formation of the silicon dioxide films.

[0021]

As apparent from examples described later, the silicon dioxide film forming system in this embodiment is capable of forming wafers W, each having a high intrasurface thickness uniformity and a high interwafer thickness uniformity. This may be considered to be due to the following reasons. The process gas (a mixture of oxygen gas and hydrogen chloride gas) is heated by the heating unit 2 to, for example, about 1000°C, so that steam is generated. The temperature of the process gas slightly drops while the process gas is flowing through

the secondary gas supply pipe 5 after being heated. However, the amount of thus generated steam does not decrease even if the temperature of the process gas drops; that is, in the above equation, equilibrium of the chemical reaction of oxygen and hydrogen to produce steam does not shift toward the side of the product. Therefore, process gas does not produce steam any further in the reaction tube 31 after steam has been produced at a temperature higher than the process temperature in the reaction tube 31.

[0022]

Thus, the generation of steam has been substantially terminated before the process gas flows into spaces between the wafers W held on the wafer boat 4. Therefore, the amount of steam contained in the process gas flowing from the periphery toward the center of each wafer W remains substantially constant regardless of position thereof, and hence the film formation promoting effect of steam on all parts of the surfaces of the wafers W held in an upper part of the wafer boat 4 is substantially the same. Consequently, a film having a high intrasurface thickness uniformity can be formed. When the process gas is supplied by the conventional process gas supplying method, the generation of steam increases progressively toward the lower part of the wafer boat 4, and hence films of unsatisfactory intrasurface thickness uniformity are formed on the wafers W held in the upper part of the wafer boat 4 while films of higher intrasurface thickness uniformity are formed on the wafers W held in the lower part of the wafer boat 4. When the process gas is supplied by a process gas supplying method according to the present invention, an atmosphere that has been created by the conventional process gas supplying method in a lower part of the wafer boat 4 can be created in both upper and lower parts of the wafer boat 4. Consequently, films can be formed on the wafers W held on the wafer boat 4 in high interwafer thickness uniformity.

[0023]

More strictly, it is considered that the steam concentration of the process gas decreases as the process gas flows toward the center of the wafer W because the steam contributes to the promotion of film formation. However, as mentioned in "Description of the Related Art" above, the temperature of a central part of the wafer W is higher than that of a peripheral part of the same, and hence there is a tendency for the thickness of

the film formed on the wafer W to increase from the periphery toward the center of the wafer W. The relatively high film formation promoting effect of steam around the periphery of the wafer W contributes to increasing the thickness of a part of the film on the peripheral part of the wafer W and, consequently, the intrasurface thickness uniformity of the film may be further improved.

[0024]

The effect of progressive steam generation in the reaction tube 3 on the intrasurface thickness uniformity and the interwafer thickness uniformity is greater under lower temperatures. Thus, this embodiment can greatly contribute to the reduction of the process temperature.

[0025]

A compound gas containing hydrogen and chlorine other than the hydrogen chloride gas may be used. For example, dichlorosilane gas ( $\text{SiH}_2\text{Cl}_2$  gas) may be used instead of the hydrogen chloride gas. The step of producing water by supplying energy to the process gas is not limited to the step of heating the process gas by the heating unit 2. Water may be produced by a step wherein the process gas is activated by supplying energy to the process gas with, for example, power of microwaves or a laser beam. In that case too, preferably, steam is generated in advance before the process gas is supplied into the reaction tube such that steam is not generated any further after the process gas has been supplied into the reaction tube. Further, the oxidation process for oxidizing wafers in the reaction vessel may be carried out by a single-wafer thermal processing system, instead of a batch thermal processing system.

[0026]

[Examples]

Results of experimental film forming operations with the foregoing silicon dioxide film forming system will be described hereinafter.

[0027]

(Example 1)

Silicon dioxide films were formed on the surfaces of 20 cm diameter wafers under the following process conditions, respectively.

[0028]

Temperature in reaction tube: 800°C  
Flow rate of gases: O<sub>2</sub>/HCl = 10/0.5 slm  
Processing time: 90 min  
Temperature of heating unit: 1000°C  
Number of wafers on wafer boat: 100  
Pressure in reaction tube: -49 Pa (-5 mmH<sub>2</sub>O)

The thickness of silicon oxide films formed on the wafers in upper, middle and lower parts, respectively, of the wafer boat was measured to examine the intrasurface thickness uniformity of the silicon dioxide films. In addition, silicon dioxide films were formed on the surfaces of wafers under process conditions similar to the foregoing process conditions, except that the heating element of the heating unit was not energized. Fig. 4 shows the measured results. Intrasurface thickness uniformity is represented by a value calculated by using:

$$2 \times \text{Mean intrasurface thickness} / (\text{Maximum value} - \text{Minimum value})$$

[0029]

As obvious from Fig. 4, supplying the process gas after heating the same into the reaction tube improves the intrasurface thickness uniformity of the silicon dioxide films formed on the wafers in the upper and the middle parts of the wafer boat and improves the interwafer thickness uniformity as well.

[0030]

(Example 2)

Silicon dioxide films were formed on the surfaces of 20 cm diameter wafers under the following process conditions, respectively.

[0031]

Temperature in reaction tube: 800°C  
Flow rate of gases: O<sub>2</sub>/HCl = 10/0.3 slm  
Temperature of heating unit: 1000°C  
Number of wafers on wafer boat: 100  
Pressure in reaction tube: -49 Pa (-5 mmH<sub>2</sub>O)

Oxidation processing times were set to 2, 15, 30, and 60 min, and intrasurface thickness uniformity of the wafers held in a middle part of the wafer boat was examined. Interwafer thickness uniformity was also examined. Fig. 5 shows the results of examinations. Interwafer thickness uniformity is represented by a value calculated by using:

$$2 \times B/A$$

where A is the difference between the maximum and the minimum among the respective mean thicknesses of the silicon dioxide films formed on the wafers held on the wafer boat (practically, a predetermined number of monitor wafers held on the wafer boat) and B is the mean of the respective mean thicknesses of the silicon dioxide films formed on the wafers.

[0032]

As obvious from Fig. 5, the longer the processing time, i.e., the greater the film thickness, the greater the effect on the improvement of the intrasurface thickness uniformity and the interwafer thickness uniformity. Especially, the intrasurface thickness uniformity and the interwafer thickness uniformity may be improved even in a thin range of about 3 nm of the film thickness.

[0033]

(Example 3)

An empty wafer boat was loaded into the reaction tube, the interior of the reaction tube was heated to 800°C, and flow amounts of gasses were set to O<sub>2</sub>/HCl = 10/1 (slm). The hydrogen concentration of the gas discharged through the exhaust pipe was measured while the system was operating with the temperature of the heating unit set at 1000°C and with the heating unit turned off.

[0034]

Fig. 6 shows the measured results, in which preparatory time signifies a length of time for which the gas was supplied before starting analysis. It is known from Fig. 6 that the hydrogen concentration of the discharged gas is small when the process gas is heated with the heating unit turned on. It is inferred that the reaction:  $H_2 + 1/2 O_2 \rightarrow H_2O$  is promoted when the process gas is heated, therefore H<sub>2</sub> (hydrogen) concentration

is small. Further, when the heating unit is turned off, the above reaction is not promoted in comparison to the case where the process gas is heated with the heating unit turned on and it is therefore assumed that the H<sub>2</sub> density is high.

[0035]

#### [Advantages of the Invention]

As apparent from the foregoing description, the present invention provides the oxidation processing method and the oxidation processing system capable of obtaining high thickness uniformity of oxide films when objects to be processed are under the dry oxidation and contributing to reduction of process temperature.

#### [Brief Description of the Drawings]

[Fig. 1]

A longitudinal sectional view of an oxidation processing system used in an oxidation processing method according to the present invention.

[Fig. 2]

An outer end view of a vertical thermal processing unit used in the oxidation processing system shown in Fig. 1.

[Fig. 3]

A sectional view of a heating unit used in the oxidation processing system shown in Fig. 1.

[Fig. 4]

A view showing properties as results of investigating thickness uniformity of films at different positions on a wafer boat.

[Fig. 5]

A view showing properties as results of investigating the relationship between oxidation times and thickness uniformity of films.

[Fig. 6]

A view of assistance in explaining measurement results of hydrogen concentrations at an exhaust port of a reaction tube when a process gas is heated and not heated by the heating unit.



[Fig. 7]

A view of assistance in explaining problems of a conventional oxidation processing method.

[Reference Signs]

- 1: Vertical thermal processing unit
- 2: Heating unit
- W: Semiconductor wafer
- 20: Transparent quartz glass beads
- 21: Heating pipe
- 22: Heating element
- 23: Insulating member
- 3: Thermal processing furnace
- 31: Reaction tube
- 32: Heating element
- 4: Wafer boat
- 40: Boat elevator
- 44: Lid
- 5: Gas supply pipe
- 53: Oxygen gas source
- 54: Hydrogen chloride gas source

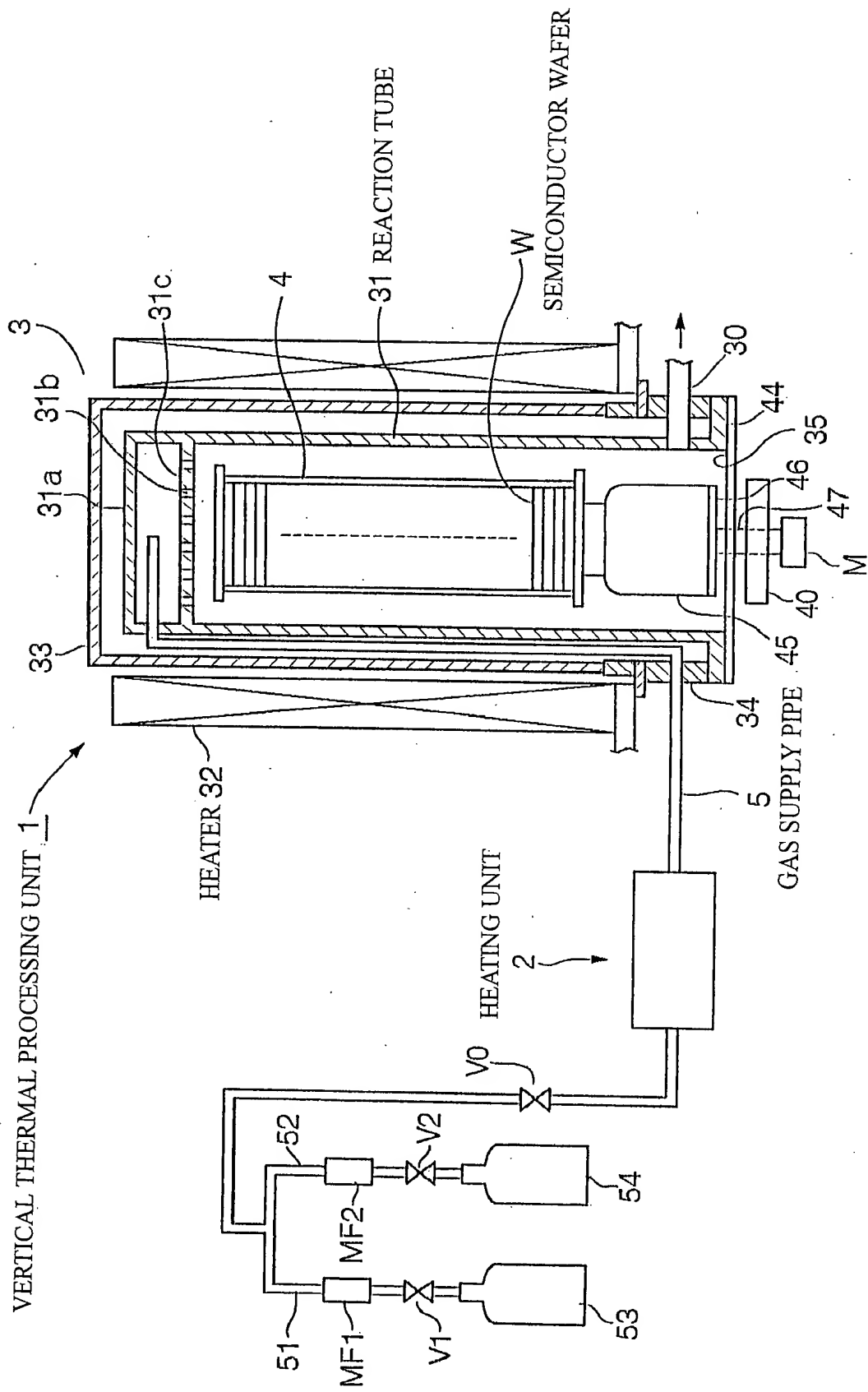


Fig. 1

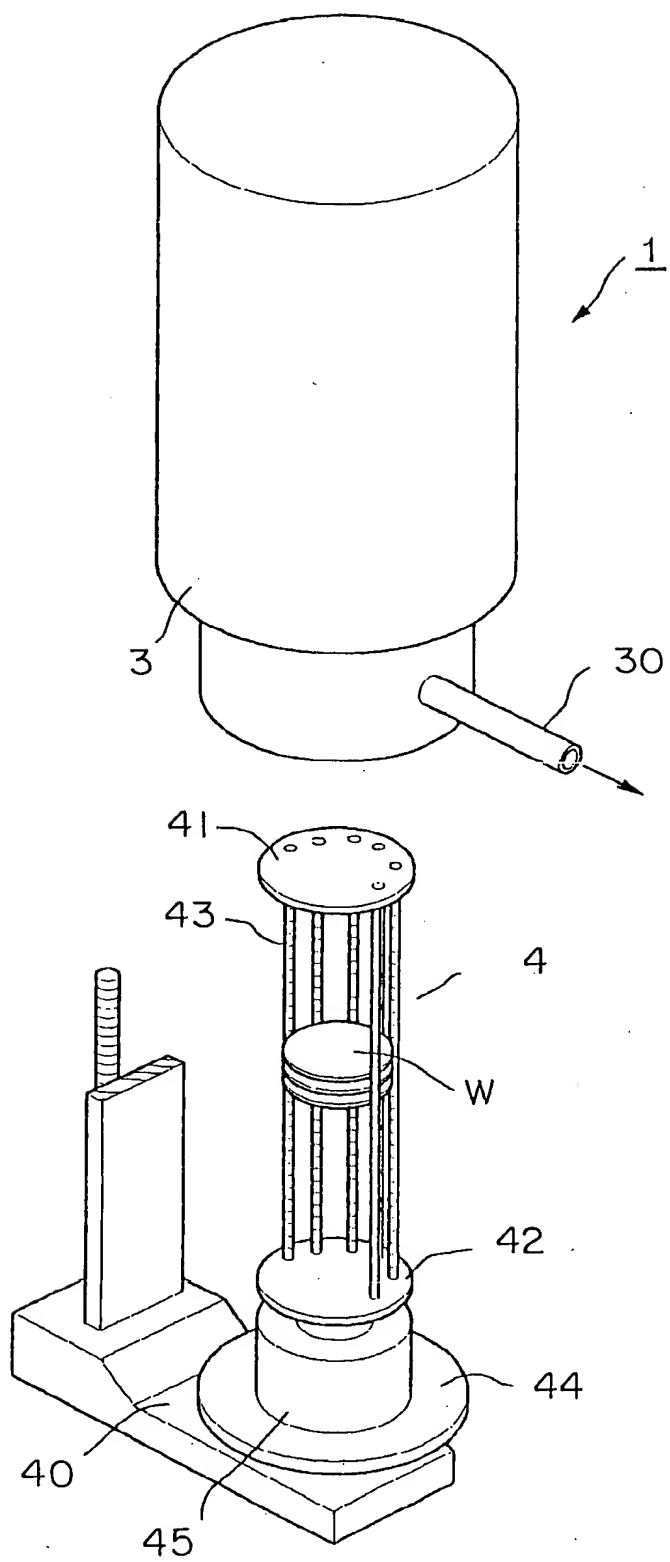


Fig. 2

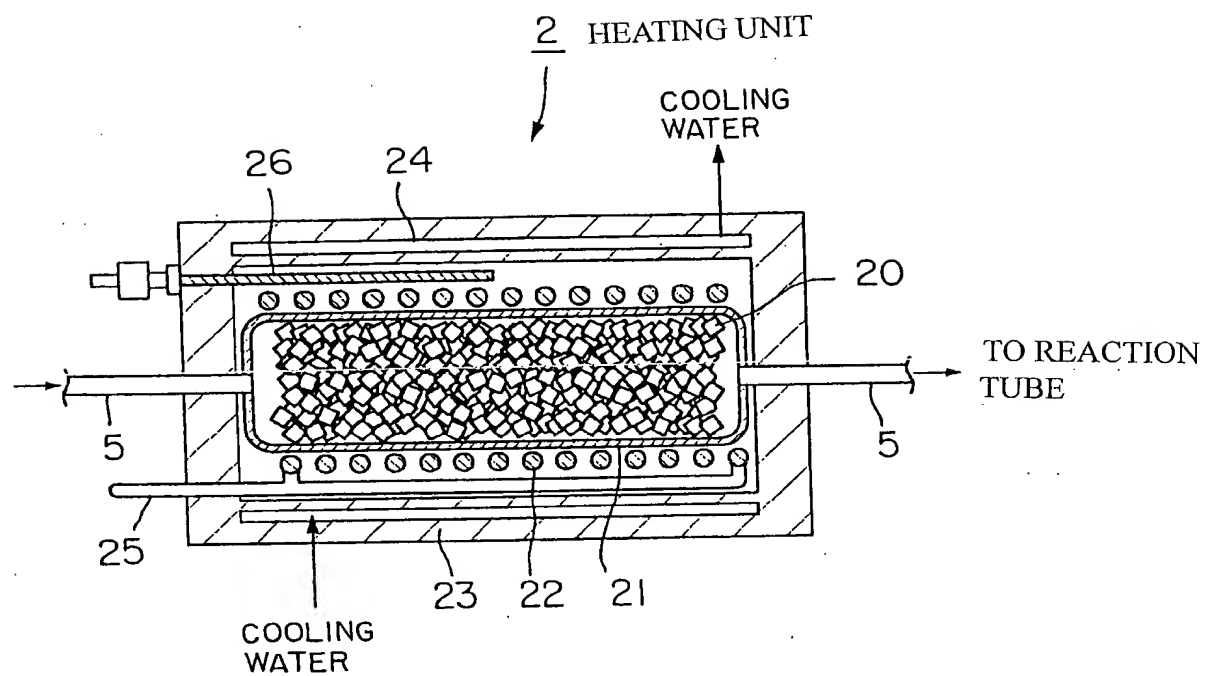


Fig. 3

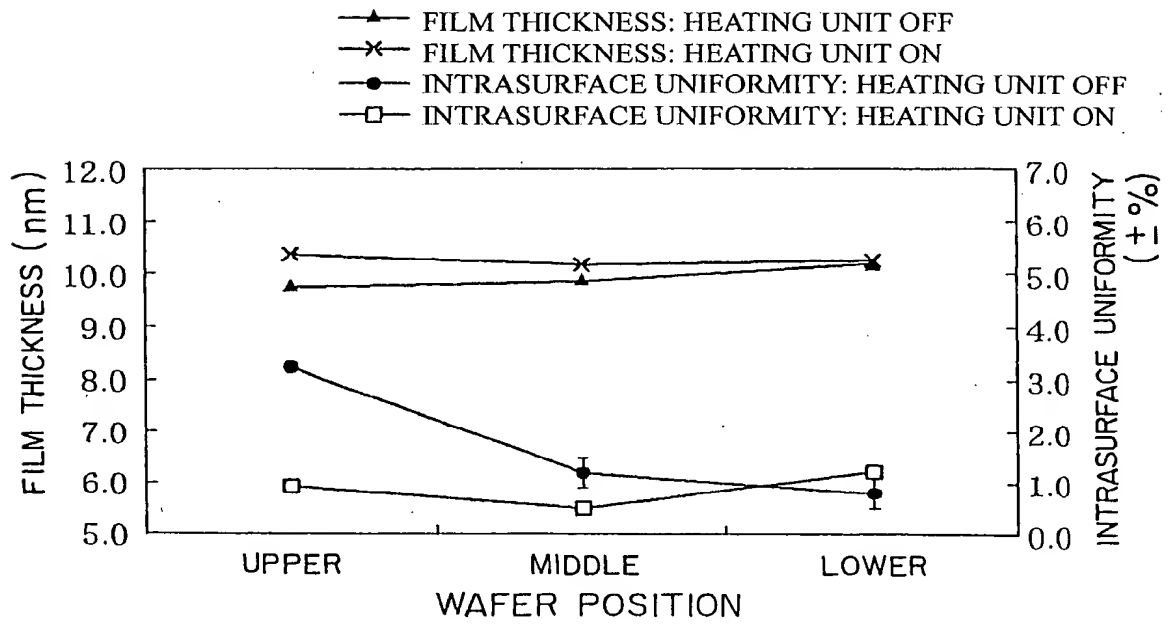


Fig. 4

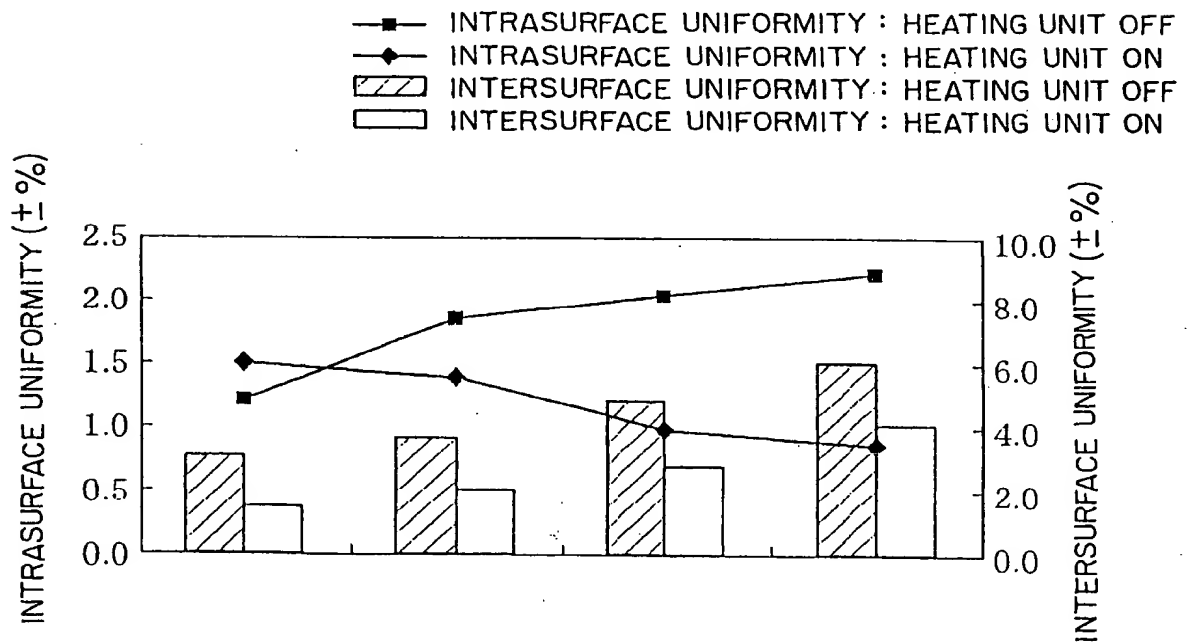


Fig. 5

Test No.	HEATING UNIT	ANALYSIS STARTING TIME (min)	H <sub>2</sub> DENSITY (ppm)
①	ON	30	<5
②		50	<5
③	OFF	30	23
④		50	78
⑤		70	24

Fig. 6

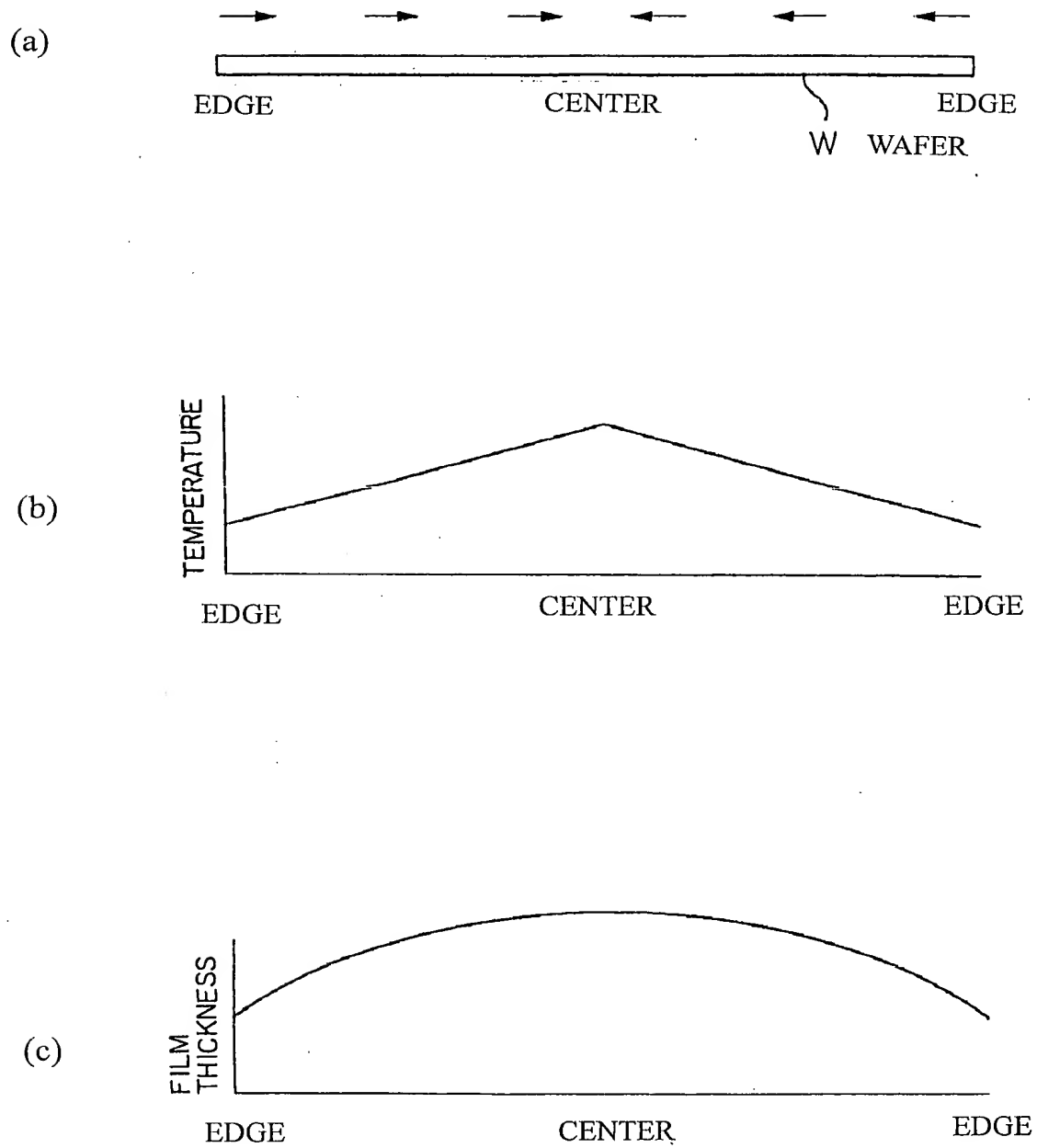


Fig. 7

[Document Name]      ABSTRACT

[Abstract]

[Means to Solve Problems]

To solve the problem that a thickness uniformity of a film becomes worse when a process temperature is low when carrying out dry oxidation wherein, for example, a silicon oxide film is formed by supplying an oxygen gas and a hydrogen chloride gas into a reaction tube of a vertical thermal processing unit to oxidize a silicon layer on a semiconductor wafer.

[Means for Solving the Problems]

A heating unit is provided in a halfway of a gas supply pipe extending outside a vertical thermal processing unit to heat a compound gas including an oxygen gas and a hydrogen chloride gas to be supplied into a reaction tube. For example, when a process temperature in the reaction tube is 800°C, the compound gas is heated to 1000°C to make the oxygen gas and the hydrogen gas react to each other to generate a small amount of water. Water is effective to increase of silicon oxide film. For example, when water is generated beforehand in a nearly balanced state, water flowing from a periphery of a wafer toward a center of the same can be prevented from being changed in an amount depending on a position within the surface of the wafer resulting in improvement of an intrasurface thickness uniformity.

[Selected Drawing]

Fig. 1